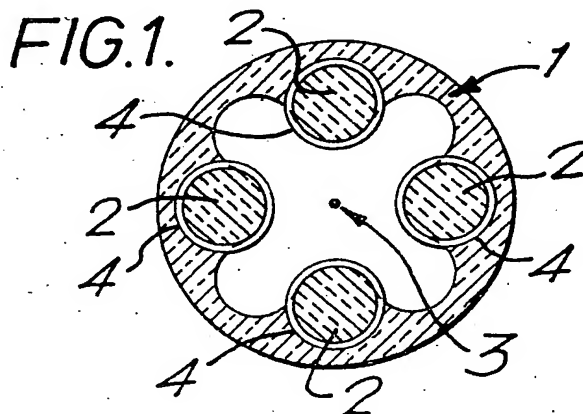


(12) **UK Patent Application** (19) **GB** (11) **2 099 216 A**

(21) Application No 8214912
(22) Date of filing 21 May 1982
(30) Priority data
(31) 8115796
(32) 22 May 1981
(33) United Kingdom (GB)
(43) Application published
1 Dec 1982
(51) INT CL³
H01J 49/02
(52) Domestic classification
H1D 21B 21C 51 7X
(56) Documents cited
GB 0918693
GB 0775656
(58) Field of search
H1D
(71) Applicants
VG Gas Analysis Limited,
Nat Lane,
Winsford,
Cheshire CW7 3QH.
(72) Inventors
Adrian Perrin Janssen.
(74) Agents
Frank B Dehn and Co.,
Imperial House,
15/19 Kingsway,
London WC2B 6UZ.

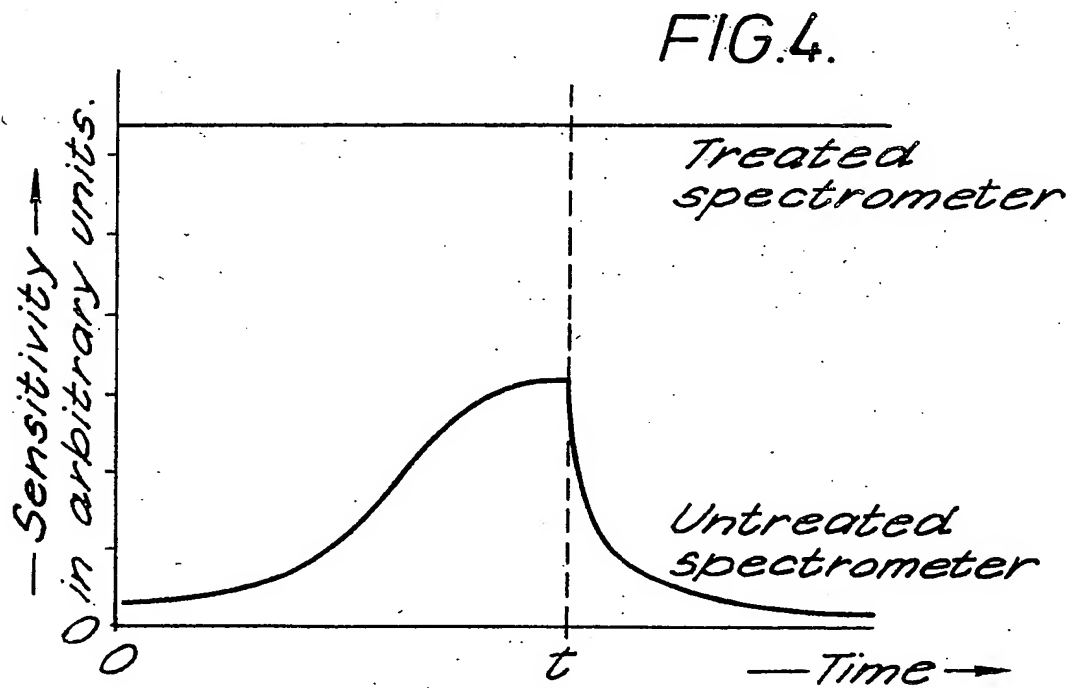
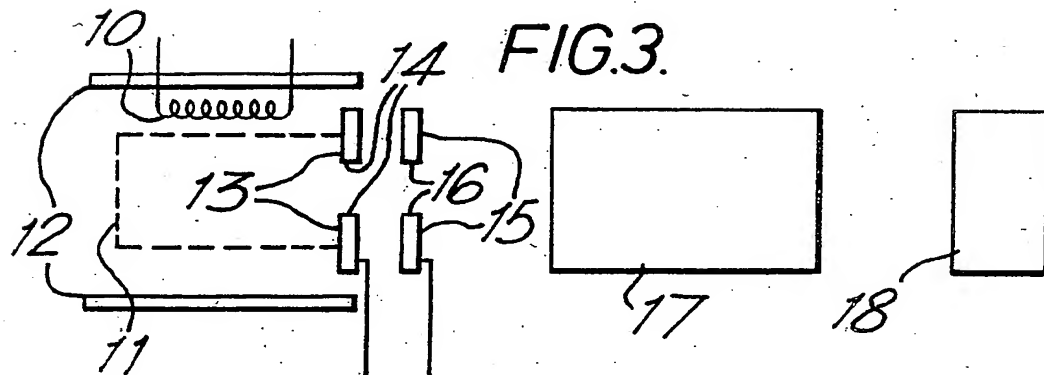
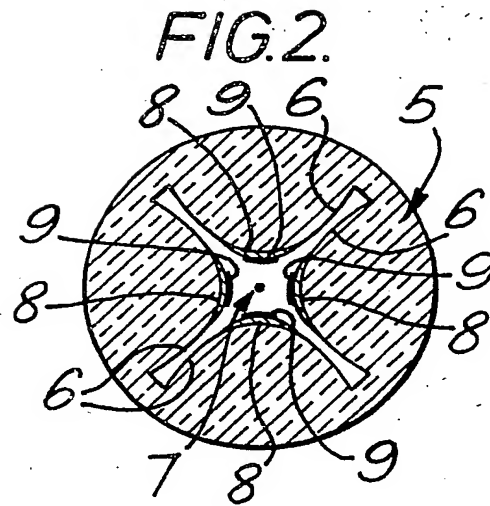
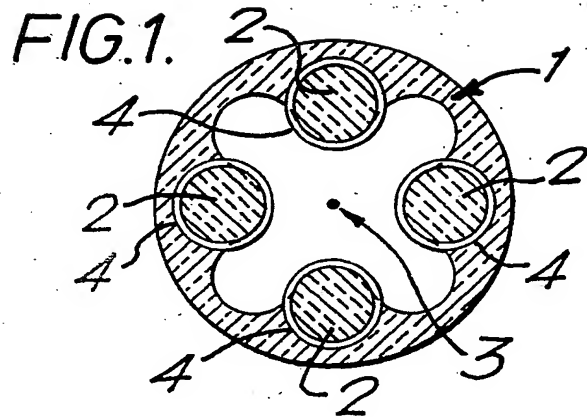
(54) **Method and coating for enhancing performance of mass spectrometers**

(57) The invention relates to a method of enhancing the performance of a mass spectrometer, in particular a quadrupole mass spectrometer, by providing a chemically inert, substantially uniform conductive coating for example of amorphous carbon to one or more of those surfaces of the components of the spectrometer which in use are capable of affecting the electrostatic fields present in the spectrometer, whereby inhomogeneities in the said fields and the magnitudes of undesired fields are reduced by reducing contamination of those surfaces by gaseous molecules and ions.



GB 2 099 216 A

1/1



SPECIFICATION

Method and coating for enhancing performance of mass spectrometers

5

This invention relates to a method of improving the performance of mass spectrometers, in particular quadrupole mass spectrometers, and to the spectrometers and components thereof so improved.

10 In all mass spectrometers ions produced in the form of an ion beam by an ion source pass to a detector via an intermediately positioned mass selector.

In a quadrupole mass spectrometer the mass selector or quadrupole mass analyser selects the ions permitted to impinge upon the detector on the basis of their mass to charge ratio. In contrast, a magnetic analyser selects ions on the basis of their momentum and charge, while a time-of-flight mass selector analyses ion velocities.

A magnetic analyser involves the application of a magnetic field perpendicular to the ion beam causing it to be deflected by an amount dependent on the mass to charge ratio of the ions. By use of a suitably placed detector, which accepts only a narrow segment of the deflected beam, ions of a particular mass to charge ratio can be detected by selecting the strength of the magnetic field or the energy with which the ions enter the magnetic field.

30 Conversely, a quadrupole mass selector consists of four electrically conductive electrodes arranged symmetrically about and very accurately parallel to the line joining ion source to detector. The opposing pairs of electrodes are conductively joined and to one pair is applied a time-dependent potential $\phi(t)$ while to the other pair is applied the potential $-\phi(t)$ where

$$\phi(t) = U + V \cos(2\pi f t)$$

wherein t is time, U is a D.C. voltage and V is the peak voltage of a radio-frequency alternating voltage of frequency f .

The motion of an ion injected into this field approximately along the longitudinal axis of the selector is described by the Mathieu equations and is the super-position of two motions. The first is a stable oscillation about the longitudinal axis of the selector whereby the ion eventually emerges from the other end of the selector. The second is an unstable motion whereby the ion is deflected away from the longitudinal axis and towards the electrodes, the surfaces of which it may strike and so be neutralized. The particular motion of an ion is determined by the parameters V , U , f , r_0 and the mass to charge ratio of the ion, where $2r_0$ is the separation between opposing electrodes. By suitable selection of these parameters, ions of a given range of mass to charge ratio will have a stable motion and will pass through the filter. For a given size of mass selector (i.e. r_0) the value of the mass selected to pass through is dependent upon V and f .

65 The selection is, to a good approximation, independent of the ion velocity. By varying the value of V and maintaining the ratio V/U substantially constant, the range of mass to charge ratios selected is varied. As the ratio V/U is decreased, the resolving power, i.e.

70 the ability to separate adjacent mass peaks, of a quadrupole mass selector tends towards a limiting value which is largely determined by the accuracy and uniformity with which the fields produced by the quadrupoles are controlled.

75 The electrodes or rods should theoretically present a convex hyperbolic surface towards the longitudinal axis but this is frequently approximated by the use of rods of circular or near circular cross-section. The rods are normally held in position by a non-conductive support, frequently ceramic. Such a support may take the form of, for example, a precision ground ceramic ring serving to locate the rods or a shaped ceramic cylinder with convex hyperbolic interior surfaces upon which coatings of

85 metal are deposited. Common materials used in the construction of the electrodes are stainless steel, molybdenum and gold. As the electrode 'diameter' is increased sensitivity improves but greater voltages and power are required and consequently rod diameters of about 6 to 18 mm are conventional. Rod lengths of between about 100 and 250 mm, and most commonly about 125 mm, are typical.

It will be appreciated that field inhomogeneities both in the source of a mass spectrometer and in the mass selector, whether a magnetic sector or a quadrupole, will adversely affect the performance. Generally the problem is worse with quadrupole selectors because any inhomogeneity in the field has the effect of seriously depressing the spectrometer sensitivity by distorting the flight path of ions which in an undisturbed field would pass through the selector so that an undesirably high proportion of the ions is filtered out. The effect of field inhomogeneities in a magnetic sector instrument is similar, but usually smaller in magnitude unless the inhomogeneities are severe. It will be further appreciated that it is not only inhomogeneities in the electrostatic fields present in the ion source and mass selector that can adversely affect the performance, but also that, for example, the presence of an unwanted electrostatic field due to localised electrical charges building up on surfaces intended to be at earth potential situated close to the ion beam can result in a similar deterioration in performance. Such unwanted fields might result from the electrical charging of an insulating film produced by contamination of the vacuum envelope of the spectrometer where it is of necessity close to the ion beam, for example, between the poles of the magnet of a magnetic sector spectrometer.

It has long been realized that great efforts should be made to minimize or eliminate such field inhomogeneities. In particular, the parts of the spectrometer and especially of the mass selector, have been manufactured with great precision to provide an initially uniform field and have been maintained scrupulously clean to avoid surface contamination.

It should be noted that the whole instrument is sometimes filled with the sample material, while contamination by material under examination is

minimised by the fact that the instruments are operated at very low pressures (approximately 10^{-4} to 10^{-14} Torr) to ensure that the flight path from source to detector is less than the mean free path of the ions. The quadrupole surfaces are particularly sensitive to such contamination. Furthermore, in the cases where mass selectors involve an electrostatic field, electrodes have normally been fabricated with metallic surfaces which are able to disperse the charge transferred when stray ions impinge upon their surfaces, thus preventing the localized build-up of electrostatic charge. Contamination of these surfaces may reduce the ability to eliminate such localized charges. Similarly, the presence of a layer or patches of contamination which can become charged in this way on such metallic surfaces which are intended to be at earth potential, for example the vacuum envelope of the spectrometer, can also have a detrimental effect on performance due to the creation of undesired electrostatic fields by the charging of the insulating layer which can affect the path of the ion beam. This effect is most pronounced where the contaminated surface is of necessity close to the ion beam, for example, the vacuum envelope between the poles of the magnet in a magnetic sector spectrometer, or on the surface or edges of plates used to form earthed slits which define the size of the ion beam.

In practice, and particularly with quadrupole mass spectrometers, such surface contamination by gaseous molecules and ions, especially by oxidant and reductant species such as, for example, argon ions, carbon monoxide and oxygen has led to low and highly variable sensitivity and poor reproducibility of results by altering the chemical composition of the surfaces and hence the precise geometry of the applied field(s), particularly of the electrostatic field. Especially unsatisfactory results have been obtained when the redox nature of the sample species is time-dependent or when alternating between oxidant and reductant species, as is frequently the case when monitoring industrial gases.

We have surprisingly found, however, that rather than relying on the scrupulous cleaning of metallic surfaces hitherto employed, the application of a chemically inert conductive coating to at least some of the conducting surfaces within a mass spectrometer enhances the performance thereof dramatically, in particular by increasing the spectrometer sensitivity and the reproducibility of results without involving a significant decrease in the resolving power of the spectrometer. As indicated below, a preferred form of coating is amorphous carbon, for example lamp black and it is remarkable, considering in the case of a quadrupole selector the high degree of precision with which the quadrupole has to be constructed, that a relatively thick coating can be applied beneficially without particularly rigorous monitoring of the precise dimensions of the newly formed surface.

One concept of the present invention is therefore to provide a method of improving the performance of a mass spectrometer, for example a conventional mass spectrometer or a multipole mass spectrometer such as a quadrupole mass spectrometer, by

the provision to some or all of the parts thereof having conductive metallic surfaces which are capable of affecting the electrostatic fields in the spectrometer by the deliberate provision of an electrical potential to the said surfaces or by the accidental build up of electrical charges on such surfaces by their contamination with non-conducting material of a chemically inert, substantially uniform conductive coating.

According to one aspect of the present invention there is provided a method of enhancing the performance of a mass spectrometer, which method comprises providing a chemically inert, substantially uniform, conductive coating to one or more of those surfaces of the components of the spectrometer which, when the spectrometer is in use, are capable of affecting the electrostatic fields present in the spectrometer, whereby inhomogeneities in the said fields and the magnitudes of undesired fields are reduced.

According to a further aspect of the present invention there is provided a mass spectrometer having components whose surfaces are capable of affecting the electrostatic fields present in the spectrometer when in use, wherein one or more of the said surfaces are wholly or partially of a chemically inert, substantially uniform, conductive material.

According to a still further aspect of the present invention there is provided a mass spectrometer component which in use is capable of affecting the electrostatic fields present in the spectrometer having as at least part of the surface thereof a chemically inert, substantially uniform, conductive material.

The coating material referred to above should be such as to prevent or minimize localized electrostatic charge build-up which might, for example, result from the impact of ions rejected by the mass selector. It is therefore important that the coating be electrically conductive and should remain electrically uniform. Furthermore, unlike the metal surfaces commonly used as electrodes (e.g. stainless steel, molybdenum, gold, etc), it is important that the surface of the coating should be chemically passive to, for example, ion impact under the operating conditions of the spectrometer, bearing in mind the chemical reactivity of the ions of the inert gases such as argon which are commonly present in the spectrometer. Thus the surface coating should be able to minimize localized changes in the chemical composition or oxidation state of the surface. Alternatively this may be expressed as a requirement that chemical reaction or long-term chemisorption of gaseous ions or molecules on the surfaces should be minimized.

If the coating is to be applied in particulate form then, to obtain as uniform a coating as possible, it is preferable that the particles be minute and advantageously microcrystalline.

One example of such a coating as envisaged above comprises graphite, preferably in the microcrystalline or amorphous form, such as that known as lamp black.

While the coating thicknesses used in the present invention, as applied to conventional conductive surfaces, are conveniently 10^{-1} to 10^2 μm , preferably

about 10 μm , the electrodes may also consist substantially completely of the type of material used for coating, e.g. amorphous carbon.

Enhancement of mass spectrometer performance is obtained by the application of coatings of the kind discussed above to the surfaces of the electrostatic field poles within the spectrometer, and to surfaces within the spectrometer close to the ion beam. In particular, increased sensitivity and increased data reproducibility results from the application of such coatings, advantageously of amorphous carbon, to the rods of a quadrupole mass filter. The surface area coated should be symmetrically arranged about the longitudinal axis of the quadrupole selector, preferably with C_{4h} symmetry and preferably extending the entire length of the rods. Thus, while total coverage of the rods is advantageous, partial coverage extending outwards with C_{4h} symmetry from the line on each rod surface closest to the longitudinal axis of the selector is deemed sufficient to effect some enhancement of spectrometer performance. Thus, it may be possible to omit longitudinal coverage of that part of each of the rods furthest from the axis of the selector, for example up to about 40% or even up to about 70% of the surface. It should however be noted that any coverage of the non-conducting rod support should not be such as to conductively link neighbouring rods.

Independent enhancement of performance also results from the application of such coatings to the surfaces of the ion source and/or the ion lenses or collimators preceding the mass selector, and in particular to the grid and front plate of a hot filament ion source.

It is of course particularly preferable to coat according to the invention both the ion source and the poles of the mass selector. Similarly it should be realized that the coating in this fashion of other conductive surfaces (except the internal surfaces of an electron multiplier, if present) within a mass spectrometer, and especially within the vacuum envelope of the spectrometer, will provide some enhancement of the spectrometer performance.

Coating according to the invention may be achieved by dipping, spraying or sputtering techniques or, in the case of amorphous carbon coatings, by exposure of the surface to be coated to a cloud of smoke from a suitable burning carbonaceous material such as a hydrocarbon wax. Other materials deemed suitable for use in coating according to the invention include, for example, vitreous carbon and vitreous, pyrolytic and colloidal graphite.

The enhancement in performance provided by the invention may conveniently be utilized to enable spectrometer design and construction to be modified. Thus, instead of greatly increasing the sensitivity of the spectrometer, it may be preferred to make the sensitivity comparable to that of a conventional untreated spectrometer, for example by manufacturing the components of the treated spectrometer with less precision and consequently more economically. Alternatively, in the case of quadrupole mass spectrometers, quadrupole mass selectors significantly shorter in length (e.g. approximately 3 cm in length) treated according to the invention may be employed

satisfactorily or the radius r_0 hereinbefore referred to may be increased with the consequent effect of permitting a greater number of ions to traverse the selector, and so increasing detection rates and/or sensitivity.

In the use of conventional quadrupole mass spectrometers it was generally found that, on introduction of a sample, the sensitivity varied with time slowly approaching a limiting stable value. In practice, therefore, it was generally desirable to pass the ion beam from a particular sample through the instrument for a period of 30 or more minutes to equilibrate, before recording a mass spectrum. This prevented rapid changes of sample and inhibited the frequent calibration with standard samples which is normally desirable for the acquisition of accurate results. We have found that by coating the electrically conductive surfaces of the instrument, in particular of the quadrupole mass selector, the sensitivity is not only enhanced but is virtually constant following the initial exposure to the ion beam.

The accompanying Figures illustrate aspects of the invention, but should not be taken to limit the scope thereof.

In Figures 1 and 2, lateral cross sections through typical quadrupole mass selectors are shown, the area of the rod surface coated according to the invention being indicated.

In Figure 3 the area of a typical ion source coated according to the invention is indicated schematically.

In Figure 4 is shown a graph plotting against time the sensitivity of a quadrupole mass spectrometer, used in the analysis of residual gases.

At time 0 nitrogen was introduced into the ion source region and at time t (approximately 60 minutes) oxygen was introduced. The sample gas used included oxygen, nitrogen, argon, neon, helium, carbon dioxide, carbon monoxide, water vapour and low molecular weight hydrocarbons. In the case of the untreated spectrometer (the lower line in Figure 4) the drastic effects on spectrometer sensitivity of the introduction of nitrogen and oxygen, as described above, are clearly visible as are the long delay times before stabilization of spectrometer sensitivity. Conversely the sensitivity (the upper line in Figure 4) of the spectrometer in which the rods of the quadrupole mass selector and the grid and front plate of the ion source had been coated according to the invention with amorphous carbon is shown to be not only enhanced but effectively time- and sample-independent.

In the quadrupole selector shown in Figure 1, two ceramic supports (only one shown) accurately support metal rods 2 symmetrically about the longitudinal axis 3. Each of the rods is completely covered with a coating of lamp black 4.

In the quadrupole selector shown in Figure 2, a ceramic cylinder 5 is accurately pierced to provide four inward facing convex hyperbolic surfaces 6 symmetrically positioned with respect to the longitudinal axis 7. A portion of each hyperbolic surface is coated with metal 8 and carries a further coating of lamp black 9.

In the hot filament source shown in Figure 3, a hot

filament 10 is positioned outside a cylindrical grid 11, being surrounded by a cylindrical reflector 12. A front plate 13 having an aperture 14 of appropriate diameter is connected to the grid 11. A focus plate 15 is spaced from the front plate 13, its aperture 16 and the reflector 12, grid 11 and aperture 14 being concentric. In operation, the grid 11 and front plate 13 are given a positive potential of about 5 volts, while the reflector 12 is given a negative potential of about 65 volts. The focussing plate will be at a slightly more negative potential. When a gas sample is introduced at high vacuum, a narrow beam of relatively low energy positive ions is produced along the axis of the system. After passing through a mass selector 17 for example as shown in Figure 1, the beam of selected ions passes to a detector 18, which may, for example, be a Faraday plate or an electron multiplier. All the exposed surfaces of the grid 11, reflector 12, plates 13 and 15 and the rods of the selector 17 are coated with lamp black. The metal parts of the detector 18, with the exception of the dynode surfaces, are also advantageously coated with lamp black.

25 CLAIMS

1. A method of enhancing the performance of a mass spectrometer, which method comprises providing a chemically inert, substantially uniform, conductive coating to one or more of those surfaces of the components of the spectrometer which, when the spectrometer is in use, are capable of affecting the electrostatic fields present in the spectrometer, whereby inhomogeneities in the said fields and the magnitudes of undesired fields are reduced.
2. A method as claimed in claim 1 wherein the said coating comprises carbon.
3. A method as claimed in either of claims 1 and 2 wherein the said coating comprises amorphous carbon.
4. A method as claimed in claim 3 wherein the said coating is from 10^{-1} to 10^2 μm in thickness.
5. A method as claimed in any one of claims 2 to 4 wherein the said coating is applied by dipping, spraying, sputtering or by exposure of the surface to be coated to a cloud of smoke from a burning carbonaceous material.
6. A method as claimed in any one of claims 1 to 5 wherein the said coating is provided to one or more of the following components of a mass spectrometer: (a) the ion source; (b) the ion lenses or collimators; and (c) the vacuum envelope of the spectrometer between the poles of a magnetic mass selector or the rods of the quadrupole mass selector of a quadrupole mass spectrometer.
7. A mass spectrometer having components whose surfaces are capable of affecting the electrostatic fields present in the spectrometer when in use, wherein one or more of the said surfaces are wholly or partially of a chemically inert, substantially uniform, conductive material.
8. A mass spectrometer as claimed in claim 7 wherein one or more of those components whose surfaces are capable of affecting the said fields is formed wholly or partially of a chemically inert,

substantially uniform, conductive material.

9. A mass spectrometer as claimed in either of claims 7 and 8 wherein the said surfaces of a chemically inert, substantially uniform, conductive material are of amorphous carbon and are formed by exposure of the said components to a cloud of smoke from a burning carbonaceous material.

10. A mass spectrometer component which in use is capable of affecting the electrostatic fields present in the spectrometer having as at least part of the surface thereof a chemically inert, substantially uniform, conductive material.

11. A component as claimed in claim 10 in the form of a quadrupole mass selector the internally facing portions of the rods of which being provided with a carbon coating of substantially C_{4h} symmetry.

12. A component as claimed in claim 10 wherein the length of the said rods is about 3 cm.

13. A mass spectrometer component as claimed in any one of claims 10 to 12 wherein the said chemically inert, substantially uniform, conductive material is amorphous carbon formed by the exposure of the said component to a cloud of smoke from a burning carbonaceous material.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1982.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.